Partitioning of manufactured Ag and CeO_2 nanoparticles in relation to soil properties

Geert Cornelis[A], Madeleine Thomas[B], Brooke Ryan[C], Jason K. Kirby[D], Douglas Beak[E], David Chittleborough[F] and Mike J. McLaughlin[G]

[A]Faculty of Sciences, University of Adelaide, Adelaide, SA, Australia, Email geert.cornelis@adelaide@edu.au
[B]Faculty of Sciences, University of Adelaide, Adelaide, SA, Australia, Email madeleine.Thomas@adelaide@edu.au
[C]Faculty of Sciences, University of Adelaide, Adelaide, SA, Australia, Email brooke.ryan@adelaide@edu.au
[D]CSIRO Land & Water, Urrbrae, SA, Australia, Email jason.kirby@csiro.au
[E]CSIRO Land & Water, Urrbrae, SA, Australia, Email doug.beak@csiro.au
[F]Faculty of Sciences, University of Adelaide, Adelaide, SA, Australia, Email david.chittleborough@csiro.au
[G]CSIRO Land & Water, Urrbrae, SA, Australia, Email mike.mclaughlin@csiro.au

Abstract

Soils are likely to be increasingly exposed to manufactured nanoparticles (MNP), but a better understanding of the influence of soil properties on their fate can improve risk assessment. The solid-liquid partitioning (K_d) and dissolution of silver (Ag) MNP and cerium oxide (CeO_2) MNP was determined after spiking soils of varying properties and compared with soluble Ag(I), Ce(III), and Ce(IV) and bulk Ag(0) and bulk CeO_2(s). In addition, MNP K_d values were determined in the same soils made sodic, after the addition of biosolids, or with increased chloride and phosphate concentrations. K_d values for MNP were mostly not significantly different than for soluble analogues but were much lower than for bulk powders. High clay content was suggested to increase K_d MNP, and especially in the presence of high Cl concentrations, 39% of added Ag MNP was dissolved. The presence of phosphate in soil suspensions decreased the K_d values in clayey soils from values higher than 10000 to values lower than 30 for CeO_2 MNP that appeared to dissolve much less than Ag MNP. The fate of Ag MNP and CeO_2 MNP in soils thus appears to be determined by more factors than have to date been investigated.

Key Words

Nanoparticles, partitioning, soil, silver, cerium.

Introduction

Ag MNP and CeO_2 MNP are amongst the most widely used MNP today (Maynard and Michelson, 2007), making use of the optical, mechanical and catalytic properties that are vastly different to more coarsely grained (bulk) powders of the same material (Klaine *et al.* 2008). The same properties can lead to toxic effects when organisms are exposed to Ag MNP and CeO_2 MNP (Navarro *et al.* 2008; Van Hoecke *et al.* 2009), but the high surface reactivity possibly result in a strong adhesion to reactive surfaces of soil solids, which potentially reduces exposure of terrestrial organisms to NP in pore water, the major exposure pathway for contaminants in terrestrial systems (e.g. Tong *et al.* 2007). The solid/liquid partitioning of Ag MNP and CeO_2 MNP is therefore of primary importance to efficiently assess their risk in soils, but has to date scarcely been investigated. Element partitioning is usually expressed as a K_d value that is calculated as $K_d = M_{solid}/[M]$ [L/kg] where M_{solid} is the geogenic or spiked element concentration expressed on a soil-weight basis (mg/kg) and [M] is the aqueous element concentration expressed on a solution volume basis (mg/L). High and low values indicate strong sorption or preferential partitioning to the soil porewater respectively. K_d values are usually related to soil properties for risk assessment (Sauve *et al.* 2000), but such relations have not yet been established in the case of Ag MNP and CeO_2 MNP. In this study, the effect of biosolid addition, sodicity and ions that form precipitates with soluble Ag or Ce forms on solid-liquid partitioning (K_d) of Ag MNP and CeO_2 MNP was investigated and NP partitioning was compared with soluble and bulk analogues. Sodicity affects 10% of arable land worldwide (Szabolcs, 1989) and predominance of sodium in porewaters is likely to increase NP dispersion (Klaine *et al.* 2008). Biosolid addition has been defined as the main exposure route of soils to NP, particularly in countries were organic-poor soils are amended with biosolids (Mueller and Nowack, 2008), that retain NP in wastewater plants (Kiser *et al.* 2009). NP interaction with dissolved organic carbon (DOC) is known to increases NP mobility in soils (Johnson *et al.* 2009). Ag(I) or Ce(III) ions are the predominant soluble Ag and Ce species in soil porewaters (Kabata-Pendias 2001) and possible formation of cerargyrite (AgCl(s), logK_s = -9.75) and monazite ($CePO_4$(s), logK_s= -26.3) may enhance Ag MNP or CeO_2 MNP dissolution, again possibly influencing their fate in soils.

Methods

Soil characterization

Four soils (0-10 cm depth) were air-dried and sieved over 2 mm. EC, pH, Total C, CEC, citrate-dithionite extractable Fe and Al and DOC and particle size analysis were determined according to standard methods (Rayment and Higginson, 1992). Total elemental Ag and Ce concentrations were determined after digestion of soil samples in aqua regia (US-EPA 3051A) and measurement by inductively coupled plasma-mass spectrometry (ICP-MS).

Ag MNP and CeO_2 MNP partitioning and dissolution

Partitioning of Ag MNP and CeO_2 MNP was determined according to Cornelis (2009). Stable Ag MNP and CeO_2 MNP were prepared by suspending 0.01 g/L Ag MNP and CeO_2 MNP in ultrapure water and 0.5 mM citrate adjusted to pH 10 with NaOH, respectively. After 3 min sonication, the suspensions were filtered with 0.20 µm filters (Sartorius) to remove large aggregates. Five replicates of 2.5 g of each soil were weighed in 50 mL centrifuge tubes to which 22.5 mL of 2.22 mM KNO_3 was added. While sonicating stock Ag MNP or CeO_2 MNP stock suspensions, 2.5 mL of suspension was added to all soil equilibrations to obtain final spike concentrations of 1.70 mg Ag/kg and 1.30 mg Ce/kg and leading to a final 2 mM KNO_3 concentration. In addition, ten replicates of 2.5 mL stock solutions were digested and analysed for total Ag and Ce to confirm MNP addition rate. The spiked suspensions were equilibrated for 24 h in an end-over-end shaker followed by centrifugation at 2100 g for 15 min. The supernatant was filtered using 0.45 µm microfiltration (MF) filters (Millipore) followed by 2 mL filtered with centrifugal ultrafiltration (UF) devices (Pall-Gellman). All UF filters and MF filters in the case of Ag were Cu-preconditioned according to Cornelis *et al.* (2009) to improve Ag and Ce recovery. Ten mL of the MF filtrates was added to open digest vessels for digestion with 65% HNO_3 and Ag or Ce determination with ICP-MS. Ag and Ce were determined in UF filtrates without prior digestion.

Partitioning of soluble Ag(I), Ce(III), Ce(IV) and bulk Ag(0) and bulk $CeO_2(s)$

2.5 g of each soil was equilibrated in 25ml of 2 mM KNO_3, or $AgNO_3$, $Ce(NO_3).6H_2O$ or $(NH_4)_2Ce(NO_3)_6$ dissolved in 2 mM KNO_3 for geogenic, soluble Ag, Ce(III) or Ce(IV) K_d determination respectively. Similar Ag and Ce spiking rates were applied for soluble as for MNP partitioning. The partitioning of bulk powders in soils was examined by adding 0.1 g of metallic Ag(0) (Fluka) or $CeO_2(s)$ (Aldrich) powders to five replicates of 50 g of each soil, equilibrated with 500 mL of 2 mM KNO_3 which resulted in addition rates of 2027 mg/kg Ag and 2462 mg/kg CeO_2. Partitioning determination was executed as described above.

Partitioning and biosolid addition

Biosolids were sampled at Bolivar Wastewater Treatment Plant, South Australia, and dried for 30 min at 60 °C and sieved to < 2 mm (53.5% moisture content). 0.1g (dry weight) was added to 2.5 g of each soil, which is the equivalent to 80 t/ha or approximately 5 years of application (Clapp and Larson 1994). Partitioning determination was executed as described above.

Effect of precipitation on partitioning

The same method and NP spiking rate AgMNP as above was used, but the background electrolyte was 100 mM KCl in case of Ag NP and 0.016 mM K_2HPO_4 in case of CeO_2 instead of 2 mM KNO_3. The chosen Cl^- and PO_4^{3-} represent the upper limit and an average concentration respectively of concentrations commonly found in soils (McLaughlin *et al.* 1997; Sims and Pierzynski 2005).

Partitioning in sodic soils

Sodicity was induced by leaching 80 g of each soil with a solution containing 2.9 mM NaCl and 0.15 mM $CaCl_2$. Leaching was initiated with 40 mL followed by two times 15 mL after 2h time intervals. 24h after the last leaching step, the soils were dried for 24 h at 30 °C. Sodium adsorption ratios (SAR) were determined by shaking 5g dry soil for 1 hour with 25 mL water. After filtration with a Whatman No.. 42 filter, 1 mL of the filtrate was mixed with 1 mL strontium chloride ($SrCl_2$) to induce clay flocculation. Sodium concentration was measured in the supernatant with a Flame photometer and Ca and Mg were measured with Atomic Adsorption Spectroscopy. Partitioning determination of Ag MNP and CeO_2 MNP was subsequently executed as described above.

Results

Table 1 shows varying properties for the soils used in this study, but overall a low carbon content. Clarke Hill and Tully soil were used exclusively for studying Ag MNP and CeO_2 MNP respectively. Figure 1 shows measured nanoparticulate (calculated as the difference in the 0.45 µm - 1kDa filtrates) and truly dissolved (<1kDa) Ag and Ce concentrations that were used to calculate the indicated K_d values. Within this limited set of soils, Ag MNP K_d values appear to increase with the clay content and extracted Al and Fe, but not apparently with other soil parameters such as pH. This relation is less clear in the case of CeO_2 MNP, but for both NP, K_d is particularly low in the sandy MC soil, which suggests together with a previous report (Fang *et al.* 2009) that MNPs collision with naturally occurring colloids may lead to aggregates larger than 0.45 µm. As the biosolids contained 39.5% clay, some K_d values were higher after biosolid addition, but the observed increase in DOC (data not shown) possibly stabilised NP suspensions (Johnson *et al.* 2009) leading to K_d decreases especially in the soils that were already quite clayey. Chloride induced dissolution of Ag MNP, possibly due to $AgCl_4^{3-}$ complexation, but even though dissolved MNP were not included in K_d calculations (Cornelis *et al.* 2009), K_d values were lowered in the presence of chloride. In the case of CeO_2 MNP, phosphate addition decreased K_d values as well, but no dissolution was observed. Surface complexation of phosphate anions on CeO_2 MNP, increasing its charge and suspension stability, might explain the particularly low K_d values. Sodicity treatments increased SAR ratios from < 0.3 to 8.4 (MC), 2.7 (Em), 3.7 (CH) and 12.4 (Tu), but even though a sodium predominance has been reported to increase NP transport in porous columns (Saleh *et al.* 2008), the effect on partitioning in this study remains unclear. Figure 2 shows that partitioning of bulk powders added to soil were much higher than nanoparticulate analogues as well as soluble Ag(I), Ce(III) or Ce(IV). Soluble Ag(I) partitioning did not differ significantly from Ag NP partitioning and CeO_2 partitioning was only significantly lower in MC soil, which can possibly be attributed to the high clay percentage in both Em, CH and Tu soils, but differences in clay percentage apparently did not result in differences in partitioning between Ag MNP and soluble Ag(I).

Table1. Soil chemical and physical properties

				Citrate – dithionite ext		Particle Size Analysis		
Soils	EC dS/ cm	pH	Total C %	Al mg/kg	Fe mg/kg	Clay %	Silt %	Sand %
Mount Compass (MC)	0.01	5.20	0.1	< 100	< 100	1	0	99
Emerald Black (Em)	0.1	7.49	0.9	1410	11300	59	14	27
Clarke Hill (CH)	0.1	5.27	4.9	7850	8300	28	40	32
Tully (Tu)	0.3	5.00	2.75	6320	700	32	11	57

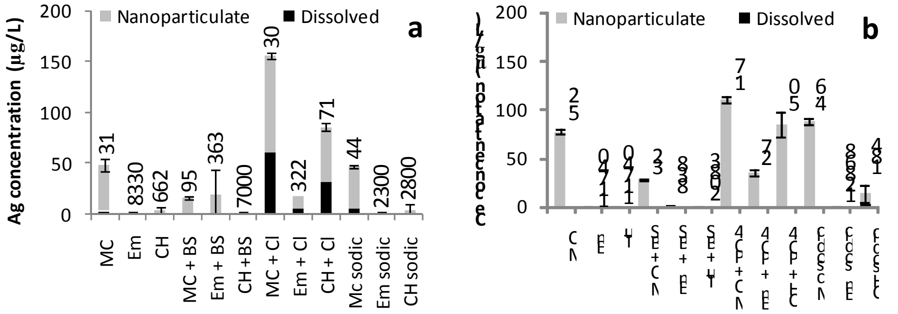

Figure 1. Measured metal concentrations in <1kDa (dissolved) and <0.45 µm filtrates (dissolved + nanoparticulate) after addition of a) Ag MNP and b) CeO_2 MNP to soils in Table 1 with increased sodicity ("sodic"), additional biosolids ("+ BS") or addition of chloride ("+ Cl") or phosphate ("+ PO_4"). Error bars are standard deviations (n=4). K_d values calculated from these concentrations are indicated as well.

Conclusion

Even though the present study should be extended towards a larger number of soils and treatments, it suggests that Ag MNP and CeO_2 MNP are mobile in soils despite their high surface reactivity. Moreover, their fate is determined by more factors than just pH, ionic strength and DOC concentration as suggested by previous reports. Texture was suggested to be a key soil property in determining the fate of these NP and the overall higher solubility of Ag MNP is suggests that these NP will be completely dissolved on the long term, especially in saline (high Cl) soils. In addition, surface complexation of CeO_2 MNP can influence partitioning tremendously. To allow an efficient risk assessment of Ag MNP and CeO_2 MNP, their partitioning needs to be investigated in a wide range of soils and porewater conditions, with an emphasis on MNP dissolution in conditions.

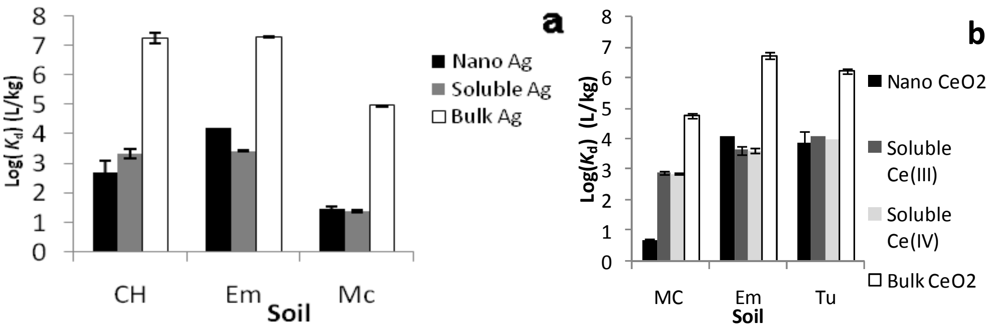

Figure 2. LogK_d values of a) Ag MNP compared with soluble Ag(I) and bulk Ag(0) and b) CeO_2 MNP compared with soluble Ce(III) and Ce(IV) and bulk CeO_2(s). Error bars are standard deviations (n=4).

A partitioning experiment with a 1.30 mg/kg soluble Ce(III) addition in the presence of phosphate resulted in K_d values higher than 10^4 L/kg in all soils probably due to monazite formation. The K_d decrease of CeO_2 MNP upon phosphate addition in Figure 1b can thus not be related to behaviour of soluble Ce(III).

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